

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-249299

(43)Date of publication of application : 28.09.1993

(51)Int.Cl.

G21K 4/00

(21)Application number : 04-083191

(71)Applicant : KONICA CORP

(22)Date of filing : 05.03.1992

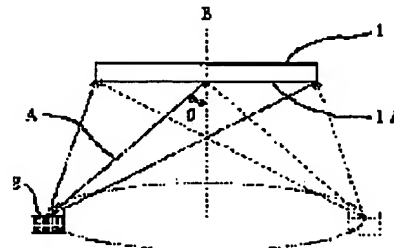
(72)Inventor : AMITANI KOJI
HONDA SATORU

(54) METHOD FOR FABRICATING RADIATION IMAGE CONVERSION PANNEL

(57)Abstract:

PURPOSE: To obtain a method for fabricating a radiation image conversion panel, by which a stimuable phosphor layer consisting of columnner crystal with narrow width and good accuracy is formed, the panel being superior in sharpness of radiation image and the panel having small sharpness change in the reading direction.

CONSTITUTION: In a method for fabricating radiation image conversion panel, includes a process of forming at least one layer of stimuable phosphor layer on the evaporated surface 1A of a base plate 1, by piling the gas phase of the accelerated fluorescent material using steam flow. The direction of the steam flow is turned around the tangential line on the evaporated surface 1A of the base plate 1 during piling the gas phase of the stimuable phosphor layer on the evaporated surface 1A of a base plate 1.



LEGAL STATUS

[Date of request for examination] 25.02.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3130633

[Date of registration] 17.11.2000

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] In the manufacture method of a radiation image transformation panel including the process which the vacuum evaporationo-ed side of a substrate is made to carry out the gaseous-phase deposition of the accelerated-phosphorescence nature fluorescent substance, and forms much more accelerated-phosphorescence nature fluorescent substance layer in it at least using a steamy style The manufacture method of the radiation image transformation panel characterized by carrying out the gaseous-phase deposition of the accelerated-phosphorescence nature fluorescent substance in the vacuum evaporationo-ed side of a substrate while rotating the direction of a streamline of the aforementioned steamy style relatively [surroundings / of the direction of a normal of the vacuum evaporationo-ed side of the aforementioned substrate].

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the manufacture method of a radiation image transformation panel including the process which the vacuum evaporation-coated side of a substrate is made to carry out the gaseous-phase deposition of the accelerated-phosphorescence nature fluorescent substance, and forms much more accelerated-phosphorescence nature fluorescent substance layer in it at least using a steamy style.

[0002]

[Description of the Prior Art] For example, in the medical field, many radiation pictures like an X-ray picture are used for the sick diagnosis. The so-called radiography which irradiates the film which used silver salt like the time of irradiating the X-ray which penetrated the photographic subject at a fluorescent substance layer (fluorescent screen), producing the light by this, and taking the usual photograph for this light conventionally as the formation method of a radiation picture, and is developed was common.

[0003] However, by making a fluorescent substance absorb the radiation which penetrated the photographic subject as a method of taking out a direct picture from a fluorescent substance layer without using the film which applied silver salt in recent years, and exciting this fluorescent substance with light or heat energy after an appropriate time, the energy of radiation which was absorbed by this fluorescent substance and accumulated is made to emit as fluorescence, and the method of detecting and imaging this fluorescence is proposed.

[0004] For example, U.S. ***** The radiation image transformation method using a visible ray or infrared radiation as an accelerated-phosphorescence excitation light is shown in the No. 3,859,527 specification and the Provisional-Publication-No. 55-No. 12144 official report using the accelerated-phosphorescence nature fluorescent substance. This method is what uses the radiation image transformation panel in which the accelerated-phosphorescence nature fluorescent substance layer was formed on the substrate. The radiation which penetrated the photographic subject in the accelerated-phosphorescence nature fluorescent substance layer of this radiation image transformation panel is applied. Store up the energy of radiation corresponding to the degree of radiopacity of a photographic subject's each part, and a latent image is formed. By scanning this accelerated-phosphorescence nature fluorescent substance layer with accelerated-phosphorescence excitation light after an appropriate time, the energy of radiation accumulated at each part is made to emit as accelerated-phosphorescence luminescence, photo electric translation of the lightwave signal by the strength of this light is carried out, for example, and it images by the picture reproducer. It may be reproduced as hard copy or this final picture may be reproduced on the display of CRT etc.

[0005] The high thing of the rate of the absorption of radiation and an optical conversion rate ("radiosensitivity" is called below including both) is required for the radiation image transformation panel which has the accelerated-phosphorescence nature fluorescent substance layer used for such a radiation image transformation method like the case of the radiography using the above-mentioned fluorescent screen, and, moreover, the high thing of the sharp nature of a picture is required.

[0006] By the way, the sharp nature of the picture in the radiation image transformation panel using the accelerated-phosphorescence nature fluorescent substance is determined depending on the breadth within the panel concerned of accelerated-phosphorescence excitation light rather than is determined by the breadth of accelerated-phosphorescence luminescence of an accelerated-phosphorescence nature fluorescent substance. the radiation image information accumulated at the radiation image transformation panel when explained in detail -- time series -- accelerated-phosphorescence luminescence by the accelerated-phosphorescence excitation light irradiated at a certain time (t_i), since it is being and taken out Although recorded as an output from a certain pixel on the panel concerned by which lightning was improved desirably [all] and accelerated-phosphorescence excitation light was irradiated at the time (x_i and y_i) Accelerated-phosphorescence excitation light spreads by dispersion etc. within the panel concerned in a loan, and if the accelerated-phosphorescence nature fluorescent substance which exists in the outside of an irradiation pixel (x_i and y_i) is also excited, the output from a lateral field will be recorded rather than the pixel as an output from the irradiation pixel (x_i and y_i) concerned. Therefore, if accelerated-phosphorescence luminescence by the accelerated-phosphorescence excitation light irradiated at a certain time (t_i) is only luminescence from the pixel (x_i and y_i) on the panel concerned by which accelerated-phosphorescence excitation light was irradiated truly at the time (t_i), when the luminescence has what breadth, there is no influence in the sharp nature of the picture acquired. in such a situation, the radiation image transformation panel by which an accelerated-phosphorescence nature fluorescent substance layer consists of a detailed columnar crystal, for example, and its manufacture method are proposed as technology of improving the sharp nature of a radiation picture (refer to JP,61-142497,A -142500 No. and a 62-105098 official report) . According to this technology, since accelerated-phosphorescence excitation light reaches to the bottom of a columnar crystal, without dissipating out of a columnar crystal, repeating reflection within a columnar crystal for the optical inductive effect of a detailed columnar crystal, it can increase more the sharp nature of the picture by accelerated-phosphorescence luminescence. When making the vacuum evaporation side of a substrate carry out gaseous-phase deposition and making a layer form in it especially using a steamy style, in the former, a means to improve the sharp nature of a radiation picture paying attention to the direction of a steamy style is proposed by forming an accelerated-phosphorescence nature fluorescent substance layer by the slanting vacuum deposition (refer to Japanese-Patent-Application-No. No. 129996 [63 to] specification) .

[0007]

[Problem(s) to be Solved by the Invention] However, with the above-mentioned technology, since the crystal of an accelerated-phosphorescence nature fluorescent substance became the thing of the tabular which had relation in ** on the other hand, there was a problem that sharp nature changed greatly with directions of read of a radiation picture. That is, if incidence of the steamy style is carried out from across to a substrate side, the portion of the "shadow" which a steamy style cannot reach easily in a substrate side is made, and since the crystal divided by that serving as a crack is formed, the sharp nature of a picture will improve. However, in the conventional vacuum deposition, since the direction of a streamline of a steamy style was fixed to the substrate side, the portion of a "shadow" inclined, and it became the crystal of the tabular with narrow width of face from which it is not pillar-shaped and width of face differs greatly by the direction, and there was a problem in which sharp nature differs by the direction of read.

[0008] Then, the purpose of this invention can form the accelerated-phosphorescence nature fluorescent substance layer which consists of a columnar crystal with a high precision with narrow width of face, and its sharp nature of a radiation picture improves, and it is to offer the method that the small radiation image transformation panel of change of the sharp nature by the direction of read can moreover be manufactured.

[0009]

[Means for Solving the Problem] In the manufacture method of a radiation image transformation panel including the process at which the manufacture method of this invention makes the vacuum evaporation side of a substrate carry out the gaseous-phase deposition of the

accelerated-phosphorescence nature fluorescent substance, and forms much more accelerated-phosphorescence nature fluorescent substance layer in it at least using a steamy style. It is characterized by carrying out the gaseous-phase deposition of the accelerated-phosphorescence nature fluorescent substance in the vacuum evaporation side of a substrate, rotating the direction of a streamline of the aforementioned steamy style relatively [surroundings / of the direction of a normal of the vacuum evaporation side of the aforementioned substrate].

[0010]

[Function] In this invention, since the direction of a streamline of a steamy style is rotated relatively [surroundings / of the direction of a normal of the vacuum evaporation side of a substrate] in case the gaseous-phase deposition of the accelerated-phosphorescence nature fluorescent substance is carried out, a crystal turns into a detailed pillar-shaped crystal divided clearly mutually, without spreading in a tabular. That is, if the direction of a streamline of a steamy style is aslant leaned to the vacuum evaporation side of a substrate, a crystal tends to grow aslant in response to the influence of the direction of a streamline, the portion of the "shadow" which a steamy style cannot reach easily in the vacuum evaporation side of a substrate will be made, and the divided crystal to which this portion serves as a crack and is extended to some extent with an inclination in the direction of a streamline of a steamy style will be formed. Although a crystal spreads in a tabular and the detailed columnar crystal was hard to be obtained conventionally since the portion of this "shadow" was fixed, since the direction of a streamline of a steamy style is relatively rotated around the direction of a normal of the vacuum evaporation side of a substrate so that the portion of this "shadow" may not incline, by this invention, the accelerated-phosphorescence nature fluorescent substance layer which consists of a detailed columnar crystal with narrow width of face is obtained. Therefore, it excels in the sharp nature of a radiation picture, and, moreover, the small radiation image transformation panel of change of the sharp nature by the direction of read is obtained. In addition, for convenience, the direction of a streamline of a steamy style considers that an evaporation source is a point, after taking into consideration an evaporation distribution near the evaporation source, and the direction which connects this point and each point of the vacuum evaporation side of a substrate is said. Moreover, the direction of a normal of the vacuum evaporation side of a substrate shall be the direction of a normal when approximating a vacuum evaporation side to a flat surface or the curved surface of curvature regularity, and neither a partial warp, nor a wave or irregularity of a vacuum evaporation side shall be taken into consideration.

[0011]

[Example] In the example of drawing 1, a substrate 1 is placed in a fixed position with a level posture, and it is arranged so that the evaporation source 2 which consists of accelerated-phosphorescence nature fluorescent substance material in the lower part side position of vacuum evaporation side 1A of this substrate 1 can revolve around the sun. When an evaporation source 2 is evaporated by excitation meanses, such as an electron beam, and a steamy style is formed, making the direction [in / the center of vacuum evaporation side 1A / for an evaporation source 2] B of a normal revolve around the sun as a shaft, the direction A of a streamline of the steamy style concerned will rotate relatively [surroundings / of the direction B of a normal of a substrate 1]. Therefore, in vacuum evaporation side 1A of a substrate 1, the accelerated-phosphorescence nature fluorescent substance layer which the portion of the "shadow" which a steamy style cannot reach easily does not incline, and consists of a detailed columnar crystal with narrow width of face is obtained. In addition, the direction which it considers that an evaporation source 2 is a point after the direction A of a streamline of a steamy style takes into consideration the evaporation distribution by about two evaporation source for convenience, and connects this point and each point of vacuum evaporation side 1A of a substrate 1 is said as mentioned above.

[0012] In the example of drawing 2, the evaporation source 2 which consists of accelerated-phosphorescence nature fluorescent substance material is placed in a fixed position, and in the upper part side position of this evaporation source 2, it is arranged so that a substrate 1 can rotate centering on the direction B of a normal in the center [in the level surface]. When an

évaporation source 2 is vaporated by excitation meanses, such as an electron beam, and a steamy style is formed, making a substrate 1 rotat in the l vel surface centering on the direction B of a normal concerned, the direction A of a streamline of the steamy style concern d will rotate relatively [surroundings / of the direction B of a normal in the center of a substrate 1]. Therefore, the accelerated-phosphorescence nature fluorescent substance layer which consists of a detailed columnar crystal with narrow width of face is obtained.

[0013] In the example of drawing 3 , the evaporation source 2 which consists of accelerated-phosphorescence nature fluorescent substance material is fixed, and in the upper part side position of this evaporation source 2, it is arranged so that a substrate 1 can rotate centering on the direction B of a normal in the center [in an inclined plane]. When an evaporation source 2 is evaporated by excitation meanses, such as an electron beam, and a steamy style is formed, making a substrate 1 rotate in an inclined plane centering on the direction B of a normal concerned, the direction A of a streamline of the steamy style concerned will rotate relatively [surroundings / of the direction B of a normal in the center of a substrate 1]. Therefore, the accelerated-phosphorescence nature fluorescent substance layer which consists of a detailed columnar crystal with narrow width of face is obtained.

[0014] In the example of drawing 4 , while the evaporation source 2 in a circle which consists of accelerated-phosphorescence nature fluorescent substance material is placed in a fixed position with a level posture, the electron beam generator 3 is arranged and the substrate 1 is placed in a fixed position by the center section of the evaporation source 2 in a circle with the level posture in the upper part side position of this evaporation source 2. When the irradiation position of electron beam 3A from the electron beam generator 3 is moved sequential or at random in accordance with the periphery of the evaporation source 2 in a circle, an evaporation source 2 is evaporated and a steamy style is formed, the direction A of a streamline of the steamy style concerned will rotate relatively [surroundings / of the direction B of a normal of a substrate 1]. Therefore, the accelerated-phosphorescence nature fluorescent substance layer which consists of a detailed columnar crystal with narrow width of face is obtained.

[0015] In this invention, in case gaseous-phase deposition is carried out, it is desirable that the crossing angle (acute angle) (refer to drawing 1) theta of the direction A of a streamline of a steamy style and the direction of a normal of the vacuum evaporatio-no-ed side of a substrate is 80 degrees or less more greatly than 0 degree, and it is desirable that it is [5 degree or more] especially 70 degrees or less. If theta is too small, the portion of a "shadow" cannot be made easily, and the detailed columnar crystal which considers it as a crack is also hard to be formed. Moreover, if theta is too large, the adhesion force to the mechanical strength and substrate of a fluorescent substance layer will decline, and it will become easy to generate a flaw and film peeling.

[0016] moreover, as shown in drawing 5 , in case the direction A of a streamline of a steamy style is rotated relatively [surroundings / of the direction B of a normal of vacuum evaporatio-no-ed side 1A of a substrate 1] It is desirable that the crossing angle phi of the total vector C and the direction of a normal of vacuum evaporatio-no-ed side 1A in each point on vacuum evaporatio-no-ed side 1A of the steamy style vector which makes a terminal point each point to which an evaporation source 2 is made into the starting point, and the normal concerned intersects vacuum evaporatio-no-ed side 1A is 0 degrees or more 30 degrees or less. It is desirable that it is [0 degree or more] especially 10 degrees or less. Although each divided detailed columnar crystal grows in the direction of the total vector C of the steamy style vector in each point on vacuum evaporatio-no-ed side 1A with an inclination to some extent, the bias of the crack from which a steamy style produces to a "shadow" that the growth direction is close to the direction of a normal of vacuum evaporatio-no-ed side 1A (a crossing angle phi is small) by the bird clapper is small. Therefore, it enables the direction of the total vector C concerned to manufacture the small radiation image transformation panel of the difference in the sharp nature according [being close to the direction of a normal of vacuum evaporatio-no-ed side 1A (a crossing angle phi being small), and] to the reading direction of a radiation picture.

[0017] In this invention, although an accelerated-phosphorescence nature fluorescent substance layer is formed by the gaseous-phase depositing method, as a gaseous-phase depositing method,

a vacuum deposition is used preferably and an electron-beam-evaporation method and a resistance heating vacuum deposition are used especially preferably. When forming an accelerated-phosphorescence nature fluorescent substance layer by the vacuum deposition, vacuum evaporation may be performed two or more times, and the accelerated-phosphorescence nature fluorescent substance layer of multilayer composition may be formed. Moreover, in a vacuum deposition, at the time of vacuum evaporation, the need may be accepted, and a substrate may be cooled or heated. Moreover, you may heat-treat an accelerated-phosphorescence nature fluorescent substance layer after a vacuum evaporation end (annealing). moreover, a vacuum deposition -- setting -- the need -- responding -- O₂ and H₂ etc. -- gas may be introduced and reactant vacuum evaporation may be performed [0018] In the formation process of the accelerated-phosphorescence nature fluorescent substance layer by the gaseous-phase depositing method, the rate of sedimentation of an accelerated-phosphorescence nature fluorescent substance layer has the amount of desirable 0.1-50-micrometer/. If the rate of sedimentation is not much small, productivity will become low, and if the rate of sedimentation is not much large, control of the rate of sedimentation will become difficult. By the way, the portion of happen [that the rectilinear-propagation nature of a steamy style is high (there are few wraparounds) / tend] of the "shadow" which a steamy style cannot reach easily produced by carrying out incidence of the steamy style from across to a substrate side is clear, therefore its vacuum evaporation ambient-pressure force is as desirable as a low (a degree of vacuum is high) for forming the fine crystal divided by the crack. Specifically, it is desirable that the vacuum evaporation ambient-pressure force is 5x10 to 4 or less Torr, and it is more desirable that they are 5x10 to 5 or less Torr. Moreover, as for the temperature of the viewpoint which prevents the fall of the sharp nature of the picture by growing gigantic of a crystal to a substrate, in the formation process of the accelerated-phosphorescence nature fluorescent substance layer by the gaseous-phase depositing method, it is desirable that it is lower than the melting point of the quality of an emission 100 degrees C or more. Although the thickness of an accelerated-phosphorescence nature fluorescent substance layer changes with the radiosensitivity of the radiation image transformation panel made into the purpose, kinds of accelerated-phosphorescence nature fluorescent substance, etc., from a viewpoint which prevents the fall of the radiosensitivity by decline in the rate of the absorption of radiation, its 30-1000 micrometers are desirable, and its 50-500 micrometers are especially desirable. Since the rate of the absorption of radiation falls when the thickness of an accelerated-phosphorescence nature fluorescent substance layer is too small, radiosensitivity becomes bad, and since the breadth to the longitudinal direction of accelerated-phosphorescence excitation light increases when thickness is too large, the sharp nature of a picture becomes bad.

[0019] Drawing 6 and drawing 7 show typically the columnar crystal 5 of the accelerated-phosphorescence nature fluorescent substance layer 4 formed by the manufacture method of this invention, a crack 6 is formed almost equally between a columnar crystal 5 and 5, and each columnar crystal 5 has independent structure. Therefore, accelerated-phosphorescence excitation light and accelerated-phosphorescence luminescence come to advance each columnar crystal 5 with sharp directivity, and the sharp nature of a picture improves. Furthermore, sharp nature becomes almost equal, even if the reading direction of a radiation picture is a longitudinal direction (the direction of X of drawing 7) and the columnar crystal of the accelerated-phosphorescence fluorescent substance layer formed by the manufacture method of this invention is lengthwise (the direction of Y of drawing 7), since the average magnitude of a and b shown in drawing 7 does not differ greatly.

[0020] In order to prevent dispersion of the accelerated-phosphorescence excitation light by the columnar crystal 5, and to prevent the directive fall of accelerated-phosphorescence excitation light and to improve MTF (modulation transfer function of a picture), about 1-50 micrometers has respectively a dip a and good Breadth b (refer to drawing 7), and the size of a columnar crystal 5 has especially desirable 1-30 micrometers. In addition, since the columnar-crystal configuration shown in drawing 6 and drawing 7 is written typically, it does not need to be limited to these forms and does not need to be a fixed form or a fixed size over the whole fluorescent

substance layer.

[0021] Drawing 8 shows the example of concrete composition of the radiation image transformation panel manufactured by the manufacture method of this invention, and, as for a protective layer and 8, 7 is [a spacer and 9] low refractive-index layers. As a material of a substrate 1, glass, ceramics, various polymeric materials, a metal, etc. are used. Specifically, metal sheets, such as plastic film, such as ceramics, such as a sintering board of glass, such as quartz glass and a chemically strengthened glass, glass ceramics, an alumina, or a zirconia, or a cellulose acetate film, polyester film, a polyethylene-terephthalate film, a polyamide film, a polyimide film, a triacetate film, and a polycarbonate film, aluminum, an aluminum magnesium alloy, iron, stainless steel, copper, and chromium, etc. are mentioned. Substrate Although thickness changes with the quality of the materials etc., generally 100 micrometers – its 5mm is desirable, and 200 micrometers – its 2mm is especially desirable from the convenience of handling. The front face of these substrates may be a glide plane, and it is good also as a split face in order to raise adhesion with an accelerated-phosphorescence nature fluorescent substance layer. Moreover, it is good also as a split face in order to make most substrates into a glide plane and only for the periphery section to raise adhesion. In this case, the periphery section made into the split face has the desirable direction stopped into the portion which is not substantially used as a picture in respect of equalization of quality of image.

[0022] A protective layer 7 is formed in order to protect physically or chemically the accelerated-phosphorescence nature fluorescent substance layer 4. This protective layer 7 may be formed so that the accelerated-phosphorescence nature fluorescent substance layer 4 may be countered through the low refractive-index layer 9 like drawing 8 , and on an accelerated-phosphorescence nature fluorescent substance layer, the application liquid for protective layers may be applied directly, and it may form it. Moreover, you may paste up the protective layer formed separately beforehand on an accelerated-phosphorescence nature fluorescent substance layer.

[0023] When forming a protective layer 7 through the low refractive-index layer 9, as a component of the protective layer 7 concerned, a translucency is good and what can be fabricated in the shape of a sheet is used. As for a protective layer 7, it is desirable to show a high light transmittance in the latus wavelength range, in order to penetrate efficiently accelerated-phosphorescence excitation light and accelerated-phosphorescence luminescence, and 80% or more of a light transmittance is desirable. As such a material, organic high molecular compounds, such as sheet glass, such as a quartz, borosilicate glass, and chemical tempered glass, and PET, extension polypropylene, a polyvinyl chloride, are mentioned. Borosilicate glass shows 80% or more of light transmittance in [wavelength] 330nm – 2.6 micrometers, and shows a high light transmittance also in short wavelength further with quartz glass. furthermore, the front face of a protective layer 7 -- MgF2 etc. -- it is [an effect which makes the fall of sharp nature small] and is desirable, while penetrating efficiently accelerated-phosphorescence excitation light and accelerated-phosphorescence luminescence, if an acid-resisting layer is prepared The thickness of a protective layer has desirable 50–5000 micrometers, and its 100–3000 micrometers are more desirable.

[0024] When forming a protective layer 7 directly on the accelerated-phosphorescence nature fluorescent substance layer 4, as a component of the protective layer 7 concerned, cellulose acetate, a nitrocellulose, a polymethylmethacrylate, a polyvinyl butyral, a polyvinyl formal, a polycarbonate, polyester, a polyethylene terephthalate, polyethylene, a vinylidene chloride, nylon, etc. can be used. moreover, this protective layer 6 -- a vacuum deposition, the sputtering method, etc. -- SiC, SiO₂, SiN, and aluminum 2O₃ etc. -- the laminating of the mineral matter may be carried out and it may be formed In this case, the thickness of a protective layer 7 has desirable 0.1–100 micrometers, and its 1–50 micrometers are more desirable.

[0025] The low refractive-index layer 9 is formed if needed from a viewpoint which raises the sharp nature of a radiation picture further. Specifically CaF₂ (refractive indexes 1.23–1.26) and Na₃ AlF₆ (refractive index 1.35), layer; ethanol which consists of MgF₂ (refractive index 1.38), SiO₂ (refractive index 1.46), etc. (refractive index 1.36) methanol (refractive index 1.33) Diethylether (refractive index 1.35) etc. -- a refractive index is chosen from layer; which is 1

substantially like the layer; vacuum layer which consists of gases which consist of a liquid, such as layer; air, nitrogen, and an argon Especially, a gas layer or a vacuum layer is desirable. In this case, the thickness of the low refractive-index layer 9 is usually 0.05–3mm.

[0026] When it is desirable to have stuck with the accelerated-phosphorescence nature fluorescent substance layer 4 as for the low refractive-index layer 9, therefore the low refractive-index layers 9 are a liquid layer, a gas layer, and a vacuum layer then — although — the low refractive-index layer 9 — CaF_2 , Na_3AlF_6 , MgF_2 , and SiO_2 etc. — what is necessary is just to stick the accelerated-phosphorescence nature fluorescent substance layer 4 and the low refractive-index layer 9 with adhesives etc., when it uses and prepares in the inside of a protective layer 7

[0027] When setting a protective layer 7 to the accelerated-phosphorescence nature fluorescent substance layer 4 and arranging distance, the spacer 8 which encloses the accelerated-phosphorescence nature fluorescent substance layer 4 is formed between a substrate 1 and a protective layer 7. Especially if the accelerated-phosphorescence nature fluorescent substance layer 4 can be held in the state where it intercepted from external atmosphere, as a spacer 8, it will not be restricted, but glass, ceramics, a metal, plastics, etc. can be used, and, as for thickness, it is desirable that it is more than accelerated-phosphorescence nature fluorescent substance layer thickness.

[0028] Although light-thermal, mechanical, chemical, or the fluorescent substance in which the first light or accelerated-phosphorescence luminescence corresponding to the exposure of high-energy radiation is shown is said by stimulus (accelerated-phosphorescence excitation) of electric ** after the first light or high-energy radiation is irradiated to a “accelerated-phosphorescence nature fluorescent substance” in this invention The fluorescent substance in which accelerated-phosphorescence luminescence is shown by the optical-like stimulus (accelerated-phosphorescence excitation) from a practical field is desirable, and especially the fluorescent substance which wavelength shows accelerated-phosphorescence luminescence by 500nm or more accelerated-phosphorescence excitation light 1 micrometer or less is desirable.

[0029] Accelerated-phosphorescence nature fluorescent substance layer The following can be used as an accelerated-phosphorescence nature fluorescent substance to constitute.

(1) BaSO_4 [given in JP,48-80487,A] : A_x (however, A expresses at least one sort of Dy, Tb, and Tm, and x expresses the number which fills $0.001 \leq x < 1$ -mol %.) Fluorescent substance expressed.

(2) SrSO_4 [given in JP,48-80489,A] : Fluorescent substance expressed with A_x (however, A expresses at least one sort of Dy, Tb, and Tm, and x expresses the number which fills $0.001 \leq x < 1$ -mol %.).

(3) Na_2SO_4 given in JP,51-29889,A, CaSO_4 , and BaSO_4 etc. — fluorescent substance which added at least one sort of Mn, Dy, and Tb

(4) BeO , LiF and MgSO_4 , and CaF_2 etc. — fluorescent substance [given in JP,52-30487,A]

(5) $\text{Li}_2\text{B}_4\text{O}_7$ given in JP,53-39277,A : Fluorescent substances, such as Cu and Ag.

[0030] (6) Li_2O and $(\text{B}-2\text{O}_2)_x$: Cu (however, x expresses the number which fills $2 < x \leq 3$.), Li_2O and $(\text{B}-2\text{O}_2)_x$: Fluorescent substances, such as Cu and Ag (however, x expresses the number which fills $2 < x \leq 3$.) [given in JP,54-47883,A]

(7) The fluorescent substance expressed with SrS:Ce of a publication, Sm , SrS:Eu , Sm , La_2O_3 S:Eu , Sm (Zn, Cd), S:Mn , and X (however, X expresses a halogen.) by the U.S. Pat. No. 3,859,527 specification.

(8) ZnS:Cu given in JP,55-12142,A, Pb fluorescent substance.

(9) A general formula given in a 55-12142 official report is $\text{BaO-xAl}_2\text{O}_3$: Eu (however, x expresses the number which fills $0.8 \leq x \leq 10$.) Umin acid barium fluorescent substance expressed.

(10) A general formula given in a 55-12142 official report is MI O-xSiO_2 : A (however, MI expresses Mg, calcium, Sr, Zn, Cd, and Ba, A expresses at least one sort of Ce, Tb, Eu, Tm, Pb, Tl, Bi, and Mn, and x expresses the number which fills $0.5 \leq x \leq 2.5$.) Alkaline-earth-metal silicate system fluorescent substance expressed.

[0031] (11) A general formula given in a 55-12142 official report is $\text{FX:Eu}(\text{Ba}_{1-x-y}\text{Mg}_x\text{Ca}_y)^{2+}$

(however, X expresses at least one sort of Br and Cl, and x, and y and e express the number which fills $0 < x+y \leq 0.6$, $xy \neq 0$, and $10^{-6} \leq e \leq 5 \times 10^{-2}$, respectively.). Fluorescent substance expressed.

(12) This 55- A general formula given in a No. 12142 official report is $\text{LnOX} : x\text{A}$ (however, Ln expresses at least one sort of La, Y, Gd, and Lu, X expresses at least one sort of Cl and Br, A expresses at least one sort of Ce and Tb, and x expresses the number which fills $0 < x < 0.1$). Fluorescent substance expressed.

(13) A general formula given in JP,55-12145,A is $(\text{Ba}_{1-x} \text{MI}) \text{FX} : y\text{A}$ (however, MI). At least one sort of Mg, calcium, Sr, Zn, and Cd is expressed. X at least one sort of Cl, Br, and I is expressed, A expresses at least one sort of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, and Er, and x and y express $0 \leq x \leq 0.6$ and the number which fills $0 < y \leq 0.2$ Fluorescent substance expressed.

(14) A general formula given in JP,55-84389,A is $\text{BaFX} : x\text{Ce}$ and $y\text{A}$ (however, X expresses at least one sort of Cl, Br, and I, A expresses at least one sort of In, Tl, Gd, Sm, and Zr, and x and y express the number which fills $0 < x \leq 2 \times 10^{-1}$ and $0 < y \leq 5 \times 10^{-2}$). Fluorescent substance expressed.

(15) A general formula given in JP,55-160078,A is $\text{MI FX} - x\text{A} : y\text{Ln}$ (however, MI). At least one sort of Mg, calcium, Ba, Sr, Zn, and Cd is expressed. A BeO, MgO, CaO, SrO, BaO, ZnO, aluminum 2O_3 , Y_2O_3 , La 2O_3 , In 2O_3 , SiO_2 , TiO_2 , ZrO_2 , GeO_2 , SnO_2 , Nb 2O_5 , Ta 2O_5 , and ThO_2 At least one sort is expressed. Ln expresses at least one sort of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sm, and Gd, X expresses at least one sort of Cl, Br, and I, and x and y express $5 \times 10^{-5} \leq x \leq 0.5$ and the number which fills $0 < y \leq 0.2$ Rare-earth-elements activation divalent metal fluoro halide fluorescent substance expressed.

[0032] (16) The fluorescent substance with which the general formula of a publication is expressed with $\text{ZnS} : \text{A}$, $\text{S} : \text{A}$ (Zn, Cd), $\text{CdS} : \text{A}$, $\text{ZnS} : \text{A}$, X, $\text{CdS} : \text{A}$, and X (however, A expresses Cu, Ag, Au, or Mn, and X expresses a halogen.) by the 55-160078 official report.

(17) Provisional-Publication-No. 59- (PO4) 2 and $y\text{A}$ General formula given in a No. 38278 official report [I] (among a formula) $x\text{M}_3$ (PO4) 2 and $\text{NX}_2 : y\text{A}$ general formula [II] M_3M and N express at least one sort of Mg, calcium, Sr, Ba, Zn, and Cd, respectively. X at least one sort of F, Cl, Br, and I is expressed, A expresses at least one sort of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sb, Tl, Mn, and Sn, and x and y express the number which fills $0 < x \leq 6$ and $0 < y \leq 1$ The fluorescent substance expressed.

(18) general formula [] [III] given in JP,59-155487,A -- $x\text{Eu}$ and $y\text{Sm}$ $n\text{ReX}_3$ and $m\text{AX}'_2$ (among a formula) $:x\text{Eu}$ general formula [IV] $n\text{ReX}_3$ and $m\text{AX}'_2$: Re expresses at least one sort of La, Gd, Y, and Lu. A At least one sort of alkaline earth metal of Ba, Sr, and calcium is expressed. X and X' at least one sort of F, Cl, and Br -- expressing -- x and y -- $1 \times 10^{-4} < x < 3 \times 10^{-1}$ and $1 \times 10^{-4} < y < 1 \times 10^{-1}$ -- expressing -- n/m -- $1 \times 10^{-3} < n/m < 1 \times 10^{-1}$ is expressed Fluorescent substance expressed.

(19) The general formula $a\text{BaX}_2$ given in JP,2-58593,A (1-a), and BaY_2 : Fluorescent substance expressed with $b\text{Eu}^{2+}$ (X and Y express at least one sort of F, Cl, Br, and I, and are $\text{A} \neq \text{Y}$, respectively, and a and b express among a formula the number which fills $0 < a < 1$ and $10^{-5} < b < 10^{-1}$).

(20) General formula $\text{MI X} - a\text{MIIX}'_2$ and $b\text{MIIX}''_3c\text{A}$ given in JP,61-72087,A : (however, MI) At least one sort of alkali metal of Li, Na, K, Rb, and Cs is expressed. MII at least one sort of divalent metals of Be, Mg, calcium, Sr, Ba, Zn, Cd, Cu, and nickel -- expressing -- MIII At least one sort of trivalent metals of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, aluminum, Ga, and In are expressed. X, X', and X'' express at least one sort of halogens of F, Cl, Br, and I. A expressing at least one sort of metals of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu, and Mg, a, b, and c express $0 < a < 0.5$, $0 < b < 0.5$, and the number that fills $0 < c \leq 0.2$ Alkali halide fluorescent substance expressed.

[0033] In this invention, it can use preferably especially from an alkali halide fluorescent substance being suitable for a vacuum deposition. However, in this invention, after not being limited to the above fluorescent substance but irradiating radiation, when accelerated-phosphorescence excitation light is irradiated, it is the fluorescent substance in which accelerated-phosphorescence luminescence is shown, and if gaseous-phase deposition can be

carried out, other fluorescent substances can also be used.

[0034] Drawing 9 shows the outline of an example of the radiation image transformation equipment constituted using the radiation image transformation panel manufactured by the method of this invention. 10 a photographic subject and 12 for a radiation generator and 11 A radiation image transformation panel, The photoelectrical inverter which detects accelerated-phosphorescence luminescence to which 13 was emitted from the accelerated-phosphorescence excitation light source, and 14 was emitted from the radiation image transformation panel 12, The regenerative apparatus which reproduces as a picture the signal with which 15 was detected by the photoelectrical inverter 14, the display with which 16 displays the picture reproduced with the regenerative apparatus 15, and 17 are filters which accelerated-phosphorescence excitation light and accelerated-phosphorescence luminescence are separated [filters], and make only accelerated-phosphorescence luminescence penetrate. In this radiation image transformation equipment, incidence of the radiation from the radiation generator 10 is carried out to the radiation image transformation panel 12 through a photographic subject 11. This radiation that carried out incidence is absorbed by the accelerated-phosphorescence nature fluorescent substance layer of the radiation image transformation panel 12, the energy is accumulated, and the accumulation image of a radiopacity image is formed. Next, this accumulation image is excited with the accelerated-phosphorescence excitation light from the accelerated-phosphorescence excitation light source 13, and is made to emit as accelerated-phosphorescence luminescence. Since the strength of accelerated-phosphorescence luminescence emitted is proportional to the accumulated amount of energy of radiation, it can observe a photographic subject's 11 radiopacity image by carrying out photo electric translation of this lightwave signal by the photoelectrical inverters 14, such as the photomultiplier tube, reproducing as a picture with a regenerative apparatus 15, and displaying with display 16.

[0035] Hereafter, although a still more concrete example is explained, this invention is not limited to these examples.

[Example 1] As shown in drawing 1, 0.5mm and a size by 100mmx100mm [thickness] A front face consists of a smooth aluminum plate, and the substrate 1 heated by the temperature of 250 degrees C under the ambient-pressure force of 1×10^{-5} or less Torrs is placed in a fixed position with a level posture. The evaporation source 2 which is from accelerated-phosphorescence nature fluorescent substance material (RbBr: 1×10^{-4} Tl) on the lower part side of vacuum evaporation side 1A of this substrate 1 has been arranged so that it can revolve around the sun considering the direction of a normal of vacuum evaporation side 1A of a substrate 1 as a shaft. Making an evaporation source 2 revolve around the sun in the level surface centering on the direction of a normal of vacuum evaporation side 1A, the evaporation source 2 was evaporated with the electron beam, the steamy style was formed, and the accelerated-phosphorescence nature fluorescent substance layer was formed in vacuum evaporation side 1A of a substrate 1. However, the crossing angle (acute angle) theta of the direction A of a streamline of a steamy style and the direction of a normal for the vacuum evaporation side center section of a substrate was set as 45 degrees. When the obtained accelerated-phosphorescence nature fluorescent substance layer was observed with the electron microscope, it has checked that the average of a dip consisted of 7 micrometers and a detailed columnar crystal 11 micrometers and whose thickness the average of Breadth b is 250 micrometers. On this accelerated-phosphorescence nature fluorescent substance layer, the protective layer which consists of a glass plate through the low refractive-index layer which consists of dry nitrogen gas was prepared, and the radiation image transformation panel 1 was manufactured.

[0036] [Example 2] As shown in drawing 2, the evaporation source 2 which consists of the same accelerated-phosphorescence nature fluorescent substance material as an example 1 has been placed in a fixed position, and in the upper part side position of this evaporation source 2, the same substrate 1 as an example 1 has been arranged so that it can rotate centering on the direction B of a normal in the center [in the level surface]. Making a substrate 1 rotate in the level surface centering on the direction B of a normal concerned, the evaporation source 2 was

evaporated with the electron beam, the steamy style was formed, and the accelerated-phosphorescence nature fluorescent substance layer was formed in vacuum evaporation on side 1A of a substrate 1. However, the crossing angle θ was set as 45 degrees. When the obtained accelerated-phosphorescence nature fluorescent substance layer was observed with the electron microscope, it has checked that the average of a dip a consisted of 7 micrometers and a detailed columnar crystal 11 micrometers and whose thickness the average of Breadth b is 250 micrometers. The radiation image transformation panel 2 was manufactured like the example 1 below.

[0037] [Example 3] As shown in drawing 3, the evaporation source 2 which consists of the same accelerated-phosphorescence nature fluorescent substance material as an example 1 has been placed in a fixed position, and in the upper part side position of this evaporation source 2, the same substrate 1 as an example 1 has been arranged so that it can rotate centering on the direction B of a normal in the center [in an inclined plane]. Making a substrate 1 rotate in an inclined plane centering on the direction B of a normal concerned, the evaporation source 2 was evaporated with the electron beam, the steamy style was formed, and the accelerated-phosphorescence nature fluorescent substance layer was formed in vacuum evaporation on side 1A of a substrate 1. However, the crossing angle θ was set as 40 degrees. When the obtained accelerated-phosphorescence nature fluorescent substance layer was observed with the electron microscope, it has checked that the average of a dip a consisted of 8 micrometers and a detailed columnar crystal 11 micrometers and whose thickness the average of Breadth b is 250 micrometers. The radiation image transformation panel 3 was manufactured like the example 1 below.

[0038] [Example 4] As shown in drawing 4, while having placed in a fixed position the evaporation source 2 in a circle which consists of the same accelerated-phosphorescence nature fluorescent substance material as an example 1 with the level posture, the electron beam generator 3 has been arranged in the center section of the evaporation source 2 in a circle, and the same substrate 1 as an example 1 has been placed in a fixed position with the level posture in the upper part side position of this evaporation source 2. The irradiation position of electron beam 3A from the electron beam generator 3 was moved one by one in accordance with the periphery of the evaporation source 2 in a circle, the evaporation source 2 was evaporated, the steamy style was formed, and the accelerated-phosphorescence nature fluorescent substance layer was formed in vacuum evaporation on side 1A of a substrate 1. However, the crossing angle θ was set as 40 degrees. When the obtained accelerated-phosphorescence nature fluorescent substance layer was observed with the electron microscope, it has checked that the average of a dip a consisted of 8 micrometers and a detailed columnar crystal 11 micrometers and whose thickness the average of Breadth b is 250 micrometers. The radiation image transformation panel 4 was manufactured like the example 1 below.

[0039] [Example 1 of comparison] As shown in drawing 10, the evaporation source 2 which consists of the same accelerated-phosphorescence nature fluorescent substance material as an example 1 has been placed in a fixed position, and in the upper part side position of this evaporation source 2, the same substrate 1 as an example 1 has been placed in a fixed position so that it cannot rotate in the inclined plane where a crossing angle θ becomes 40 degrees. The evaporation source 2 was evaporated with the electron beam, the steamy style was formed, and the accelerated-phosphorescence nature fluorescent substance layer was formed in vacuum evaporation on side 1A of a substrate 1. When the obtained accelerated-phosphorescence nature fluorescent substance layer was observed with the electron microscope, it has checked that the average of a dip a consisted of 6 micrometers and broad plate crystal 26 micrometers and whose thickness the average of Breadth b is 250 micrometers. The radiation image transformation panel a was manufactured like the example 1 below.

[0040] [Example 2 of comparison] As shown in drawing 11, the evaporation source 2 which consists of the same accelerated-phosphorescence nature fluorescent substance material as an example 1 has been placed in a fixed position, and in the upper part side position of this evaporation source 2, the same substrate 1 as an example 1 has been arranged so that it can rotate centering on the direction B of a normal in the center [in the level surface]. However,

the vaporation source 2 has been arranged directly under the direction of a normal in the center of vacuum evaporation-side 1A of a substrate 1. Making a substrate 1 rotate in the level surface centering on the direction B of a normal concerned, the evaporation source 2 was evaporated with the electron beam, the steamy stylus was formed, and the accelerated-phosphorescence nature fluorescent substance layer was formed in vacuum evaporation-side 1A of a substrate 1. When the obtained accelerated-phosphorescence nature fluorescent substance layer was observed with the electron microscope, it has checked that it was not a columnar crystal. The radiation image transformation panel b was manufactured like the example 1 below.

[0041] The examination which actually forms a radiation picture was performed using the radiation image transformation equipment of composition of being shown in drawing 9, using respectively the radiation image transformation panels 1-4 and the radiation image transformation panels a and b for comparison which are more than evaluations, and were made and manufactured, and the sharp nature of a radiation picture was investigated as follows.

[0042] Tube voltage 80 kVp-P after sticking a CTF chart on a sharp nature radiation image transformation panel. After carrying out 10mR(s) (distance from bulb to panel : 1.5m) irradiation of the X-ray, Accelerated-phosphorescence excitation is scanned and carried out with semiconductor laser light (oscillation wavelength : 780nm, a beam diameter : 100 micrometers), and it reads as accelerated-phosphorescence luminescence to which a CTF chart image is emitted from an accelerated-phosphorescence nature fluorescent substance layer, and is a light sensitive cell. (photomultiplier tube) Photo electric translation was carried out and the picture signal was acquired. By this signal value, it is the modulation transfer function of a picture. (MTF) It investigated and the relative value estimated the sharp nature of a radiation picture. In addition, MTF is a value in case spatial frequency is 3 cycles / mm. The above result was shown in the after-mentioned table 1.

[0043]

[Table 1]

	画像の鮮鋭性 (%)	
	X方向	Y方向
実施例 1	4 4	4 0
実施例 2	4 3	4 0
実施例 3	4 2	4 0
実施例 4	4 2	3 9
比較例 1	4 5	3 5
比較例 2	2 8	2 8

[0044] According to the manufacture method of this invention, the sharp nature of a radiation picture is excellent, and moreover sharp nature seldom changes with the directions of read, but a good radiation image transformation panel is obtained also in respect of the homogeneity of quality of image so that clearly from Table 1.

[0045]

[Effect of the Invention] According to this invention, as explained to the detail above, the accelerated-phosphorescence nature fluorescent substance layer which consists of a columnar crystal with a high precision with narrow width of face can be formed, the sharp nature of a radiation picture is excellent, and since change of the sharp nature by the direction of read is small, moreover, a good radiation image transformation panel can be manufactured also in respect of the homogeneity of quality of image.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

- [Drawing 1] It is drawing showing the example of manufacture of an accelerated-phosphorescence nature fluorescent substance layer.
- [Drawing 2] It is drawing showing other examples of manufacture of an accelerated-phosphorescence nature fluorescent substance layer.
- [Drawing 3] It is drawing showing other examples of manufacture of an accelerated-phosphorescence nature fluorescent substance layer.
- [Drawing 4] It is drawing showing other examples of manufacture of an accelerated-phosphorescence nature fluorescent substance layer.
- [Drawing 5] It is explanatory drawing of the crossing angle ϕ of the total vector of a steamy style vector, and the direction of a normal of a vacuum evaporationo-ed side.
- [Drawing 6] It is the cross section having shown typically the accelerated-phosphorescence nature fluorescent substance layer which consists of a columnar crystal.
- [Drawing 7] It is the perspective diagram having shown typically the accelerated-phosphorescence nature fluorescent substance layer which consists of a columnar crystal.
- [Drawing 8] It is the cross section having shown the example of concrete composition of a radiation image transformation panel.
- [Drawing 9] It is explanatory drawing having shown the outline of an example of radiation image transformation equipment.
- [Drawing 10] It is explanatory drawing of the example 1 of comparison.
- [Drawing 11] It is explanatory drawing of the example 2 of comparison.

[Description of Notations]

- 1 Substrate 2 Evaporation Source
 3 Electron Beam Generator 4 Accelerated-Phosphorescence Nature Fluorescent Substance Layer
 5 Columnar Crystal 6 Crack
 7 Protective Layer 8 Spacer
 9 Low Refractive-Index Layer 10 Radiation Generator
 11 Photographic Subject 12 Radiation Image Transformation Panel
 13 Accelerated-Phosphorescence Excitation Light Source 14 Photoelectrical Inverter
 15 Regenerative Apparatus 16 Display
 17 Filter

[Translation done.]

(19)日本国特許庁(JP)

(12) 公開特許公報(A)

(11)特許出願公開番号

特開平5-249299

(43)公開日 平成5年(1993)9月28日

(51)Int.Cl.⁵
G 2 1 K 4/00

識別記号 庁内整理番号
N 8805-2G

F I

技術表示箇所

審査請求 未請求 請求項の数 1(全 9 頁)

(21)出願番号 特願平4-83191

(22)出願日 平成4年(1992)3月5日

(71)出願人 000001270

コニカ株式会社

東京都新宿区西新宿1丁目26番2号

(72)発明者 網谷 幸二

東京都日野市さくら町1番地 コニカ株式
会社内

(72)発明者 本田 哲

東京都日野市さくら町1番地 コニカ株式
会社内

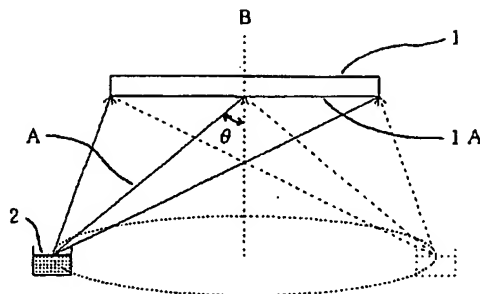
(74)代理人 弁理士 大井 正彦

(54)【発明の名称】 放射線画像変換パネルの製造方法

(57)【要約】

【目的】 幅の狭い精度の高い柱状結晶からなる輝尽性蛍光体層を形成することができ、放射線画像の鮮鋭性が優れ、しかも読み取り方向による鮮鋭性の変化が小さい放射線画像変換パネルを製造することができる方法を提供することにある。

【構成】 蒸気流を用いて基板の被蒸着面に輝尽性蛍光体を気相堆積させて少なくとも一層の輝尽性蛍光体層を形成する工程を含む放射線画像変換パネルの製造方法において、前記蒸気流の流線方向を、前記基板の被蒸着面の法線方向の回りに相対的に回転させながら、基板の被蒸着面に輝尽性蛍光体層を気相堆積させることを特徴とする。



【特許請求の範囲】

【請求項1】 蒸気流を用いて基板の被蒸着面に輝尽性蛍光体を気相堆積させて少なくとも一層の輝尽性蛍光体層を形成する工程を含む放射線画像変換パネルの製造方法において、

前記蒸気流の流線方向を、前記基板の被蒸着面の法線方向の回りに相対的に回転させながら、基板の被蒸着面に輝尽性蛍光体を気相堆積させることを特徴とする放射線画像変換パネルの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、蒸気流を用いて基板の被蒸着面に輝尽性蛍光体を気相堆積させて少なくとも一層の輝尽性蛍光体層を形成する工程を含む放射線画像変換パネルの製造方法に関するものである。

【0002】

【従来の技術】例えば医療の分野においては、病気の診断にX線画像のような放射線画像が多く用いられている。放射線画像の形成方法としては、従来、被写体を透過したX線を蛍光体層（蛍光スクリーン）に照射し、これにより可視光を生じさせてこの可視光を通常の写真を撮るときと同じように、銀塩を使用したフィルムに照射して現像する、いわゆる放射線写真法が一般的であった。

【0003】しかるに、近年、銀塩を塗布したフィルムを使用しないで蛍光体層から直接画像を取り出す方法として、被写体を透過した放射線を蛍光体に吸収させ、しかる後この蛍光体を例えば光または熱エネルギーで励起することにより、この蛍光体に吸収されて蓄積されていた放射線エネルギーを蛍光として放射させ、この蛍光を

検出して画像化する方法が提案されている。

【0004】例えば米国特許第 3,859,527号明細書、特開昭55-12144号公報には、輝尽性蛍光体を用い、可視光線または赤外線を輝尽励起光として用いた放射線画像変換方法が示されている。この方法は、基板上に輝尽性蛍光体層を形成した放射線画像変換パネルを使用するものであり、この放射線画像変換パネルの輝尽性蛍光体層に被写体を透過した放射線を当てて、被写体の各部の放射線透過度に対応する放射線エネルギーを蓄積させて潜像を形成し、しかる後にこの輝尽性蛍光体層を輝尽励起光で走査することによって各部に蓄積された放射線エネルギーを輝尽発光として放射させ、この光の強弱による光信号を例えば光電変換し、画像再生装置により画像化するものである。この最終的な画像はハードコピーとして再生されてもよいし、またはCRT等のディスプレイ上に再生されてもよい。

【0005】このような放射線画像変換方法に用いられる輝尽性蛍光体層を有する放射線画像変換パネルには、前述の蛍光スクリーンを用いる放射線写真法の場合と同様に、放射線吸収率および光変換率（両者を含めて以下

「放射線感度」と称する）の高いことが必要であり、しかも画像の鮮鋭性の高いことが要求される。

【0006】ところで、輝尽性蛍光体を利用した放射線画像変換パネルにおける画像の鮮鋭性は、輝尽性蛍光体の輝尽発光の広がりによって決定されるのではなく、輝尽励起光の当該パネル内での広がり依存して決定される。詳しく説明すると、放射線画像変換パネルに蓄積された放射線画像情報は時系列化されて取り出されるので、ある時間（ t_1 ）に照射された輝尽励起光による輝尽発光は、望ましくはすべて採光される時間に輝尽励起光が照射されていた当該パネル上のある画素（ x_1, y_1 ）からの出力として記録されるが、かりに輝尽励起光が当該パネル内で散乱等により広がり、照射画素（ x_1, y_1 ）の外側に存在する輝尽性蛍光体をも励起してしまうと、当該照射画素（ x_1, y_1 ）からの出力としてその画素よりも広い領域からの出力が記録されてしまう。従って、ある時間（ t_1 ）に照射された輝尽励起光による輝尽発光が、その時間（ t_1 ）に輝尽励起光が真に照射されていた当該パネル上の画素（ x_1, y_1 ）からの発光のみであれば、その発光がいかなる広がりを持つものであると、得られる画像の鮮鋭性には影響がない。このような状況の中で、放射線画像の鮮鋭性を改善する技術として、例えば輝尽性蛍光体層が微細の柱状結晶からなる放射線画像変換パネルおよびその製造方法が提案されている（特開昭61-142497号〜142500号、同62-105098号公報参照）。この技術によれば、輝尽励起光は、微細の柱状結晶の光誘導効果のため柱状結晶内で反射を繰り返しながら、柱状結晶外に散逸することなく柱状結晶の底まで到達するため、輝尽発光による画像の鮮鋭性をより増大することができる。特に蒸気流を用いて基板の被蒸着面に気相堆積させて層を形成させる場合は、従来において、輝尽性蛍光体層を斜め蒸着法により形成することにより、蒸気流の方向に着目して放射線画像の鮮鋭性を改善する手段が提案されている（特願昭63-129996号明細書参照）。

【0007】

【発明が解決しようとする課題】しかし、上記の技術では、輝尽性蛍光体の結晶が一方方向につながりをもった板状のものとなるため、放射線画像の読取り方向によって鮮鋭性が大きく異なるという問題があった。すなわち、蒸気流を基板面に対して斜めから入射させると、基板面において蒸気流が到達しにくい「影」の部分ができ、そこが亀裂となって区画された結晶が形成されるため画像の鮮鋭性が向上する。しかし、従来の蒸着法では、蒸気流の流線方向が基板面に対して固定化されているため「影」の部分が偏ってしまい、幅の狭い柱状ではなくて方向によって幅が大きく異なる板状の結晶となってしまい、読取り方向によって鮮鋭性がばらつく問題があった。

【0008】そこで、本発明の目的は、幅の狭い精度の高い柱状結晶からなる輝尽性蛍光体層を形成することができ、放射線画像の鮮鋭性が向上し、しかも読取り方向による鮮鋭性の変化の小さい放射線画像変換パネルを製造することができる方法を提供することにある。

【0009】

【課題を解決するための手段】本発明の製造方法は、蒸気流を用いて基板の被蒸着面に輝尽性蛍光体を気相堆積させて少なくとも一層の輝尽性蛍光体層を形成する工程を含む放射線画像変換パネルの製造方法において、前記蒸気流の流線方向を、前記基板の被蒸着面の法線方向の回りに相対的に回転させながら、基板の被蒸着面に輝尽性蛍光体を気相堆積させることを特徴とする。

【0010】

【作用】本発明では、輝尽性蛍光体を気相堆積させる際に、蒸気流の流線方向を基板の被蒸着面の法線方向の回りに相対的に回転させるので、結晶が板状に広がらずに相互に明瞭に区画された微細な柱状の結晶となる。すなわち、基板の被蒸着面に対して蒸気流の流線方向を斜めに傾けると、結晶は流線方向の影響を受けて斜めに成長しようとして、基板の被蒸着面において蒸気流が到達しにくい「影」の部分ができ、この部分が亀裂となって蒸気流の流線方向にある程度傾きながら伸びる区画された結晶が形成される。従来はこの「影」の部分が固定化されていたので結晶が板状に広がってしまい、微細な柱状結晶が得られにくかったが、本発明ではこの「影」の部分が偏らないように基板の被蒸着面の法線方向の回りに蒸気流の流線方向を相対的に回転させるので、幅の狭い微細な柱状結晶からなる輝尽性蛍光体層が得られる。従って、放射線画像の鮮鋭性に優れ、しかも読取り方向による鮮鋭性の変化の小さい放射線画像変換パネルが得られる。なお、蒸気流の流線方向とは、便宜上、蒸気源近傍での蒸気量分布を考慮した上で蒸気源を点とみなして、この点と基板の被蒸着面の各点とを結ぶ方向をいう。また、基板の被蒸着面の法線方向とは、被蒸着面を平面あるいは曲率一定の曲面に近似した時の法線方向であり、被蒸着面の部分的なそりやうねり、あるいは凹凸等は考慮に入れないものとする。

【0011】

【実施例】図1の実施例では、基板1が水平な姿勢で固定配置され、この基板1の被蒸着面1Aの下方側位置において輝尽性蛍光体材料からなる蒸気源2が公転できるように配置されている。蒸気源2を被蒸着面1Aの中央における法線方向Bを軸として公転させながら電子ビーム等の励起手段により蒸気源2を蒸発させて蒸気流を形成すると、当該蒸気流の流線方向Aが基板1の法線方向Bの回りに相対的に回転することとなる。従って、基板1の被蒸着面1Aにおいては、蒸気流が到達しにくい「影」の部分が偏ることがなく、幅の狭い微細な柱状結晶からなる輝尽性蛍光体層が得られる。なお、前述のよ

うに蒸気流の流線方向Aとは、便宜上、蒸気源2近傍での蒸気量分布を考慮した上で蒸気源2を点とみなしてこの点と基板1の被蒸着面1Aの各点とを結ぶ方向をいう。

【0012】図2の実施例では、輝尽性蛍光体材料からなる蒸気源2が固定配置され、この蒸気源2の上方側位置において、水平面内において基板1がその中央における法線方向Bを中心にして自転できるように配置されている。基板1を当該法線方向Bを軸として水平面内で自転させながら、電子ビーム等の励起手段により蒸気源2を蒸発させて蒸気流を形成すると、当該蒸気流の流線方向Aが基板1の中央における法線方向Bの回りに相対的に回転することとなる。従って、幅の狭い微細な柱状結晶からなる輝尽性蛍光体層が得られる。

【0013】図3の実施例では、輝尽性蛍光体材料からなる蒸気源2を固定し、この蒸気源2の上方側位置において、傾斜面内において基板1がその中央における法線方向Bを中心にして自転できるように配置されている。基板1を当該法線方向Bを軸として傾斜面内で自転させながら、電子ビーム等の励起手段により蒸気源2を蒸発させて蒸気流を形成すると、当該蒸気流の流線方向Aが基板1の中央における法線方向Bの回りに相対的に回転することとなる。従って、幅の狭い微細な柱状結晶からなる輝尽性蛍光体層が得られる。

【0014】図4の実施例では、輝尽性蛍光体材料からなる円環状の蒸気源2が水平な姿勢で固定配置されると共に、円環状の蒸気源2の中央部に電子ビーム発生装置3が配置され、この蒸気源2の上方側位置において、基板1が水平な姿勢で固定配置されている。電子ビーム発生装置3よりの電子ビーム3Aの照射位置を、円環状の蒸気源2の周に沿って順次またはランダムに移動させて蒸気源2を蒸発させて蒸気流を形成すると、当該蒸気流の流線方向Aが基板1の法線方向Bの回りに相対的に回転することとなる。従って、幅の狭い微細な柱状結晶からなる輝尽性蛍光体層が得られる。

【0015】本発明において、気相堆積させる際には、蒸気流の流線方向Aと、基板の被蒸着面の法線方向との交角（鋭角） θ （図1参照）が 0° より大きく 80° 以下であることが好ましく、 5° 以上 70° 以下であることが特に好ましい。 θ が小さすぎると「影」の部分ができにくく、それを亀裂とする微細な柱状結晶も形成されにくい。また、 θ が大きすぎると、蛍光体層の機械的強度や基板に対する付着力が低下してしまい、きずや膜はがれが発生しやすくなる。

【0016】また、図5に示すように、蒸気流の流線方向Aを、基板1の被蒸着面1Aの法線方向Bの回りに相対的に回転させる際には、蒸気源2を始点とし当該法線が被蒸着面1Aと交差する各点を終点とする蒸気流ベクトルの被蒸着面1A上の各点における総和ベクトルCと被蒸着面1Aの法線方向との交角 ϕ が 0° 以上 30° 以

下であることが好ましく、 0° 以上 10° 以下であることが特に好ましい。区画された各微細柱状結晶が、被蒸着面1A上の各点における蒸気流ベクトルの総和ベクトルCの方向にある程度傾きながら成長するが、その成長方向が被蒸着面1Aの法線方向に近い(交角 ϕ が小さい)ほど蒸気流が「影」になることにより生ずる亀裂の偏りが小さい。従って、当該総和ベクトルCの方向が被蒸着面1Aの法線方向に近い(交角 ϕ が小さい)ほど、放射線画像の読み取り方向による鮮鋭性の違いの小さい放射線画像交換パネルを製造することが可能になる。

【0017】本発明においては、気相堆積法により輝尽性蛍光体層を形成するが、気相堆積法としては、蒸着法が好ましく用いられ、特に、電子ビーム蒸着法、抵抗加熱蒸着法が好ましく用いられる。蒸着法により輝尽性蛍光体層を形成する場合には、蒸着を複数回行って多層構成の輝尽性蛍光体層を形成してもよい。また、蒸着法においては、蒸着時、必要に応じて基板を冷却または加熱してもよい。また、蒸着終了後に輝尽性蛍光体層を加熱処理(アニーリング)してもよい。また、蒸着法においては、必要に応じて O_2 、 H_2 等のガスを導入して反応性蒸着を行ってもよい。

【0018】気相堆積法による輝尽性蛍光体層の形成工程において、輝尽性蛍光体層の堆積速度は $0.1 \sim 50 \mu m/分$ が好ましい。堆積速度があまり小さいと生産性が低くなり、堆積速度があまり大きいと堆積速度のコントロールが困難となる。ところで、蒸気流を基板面に対して斜めから入射させることにより生ずる、蒸気流が到達しにくい「影」の部分は、蒸気流の直進性が高い(回り込みが少ない)ほど起こりやすいことは明らかであり、従って、亀裂によって区画された微細結晶を形成するには蒸着雰囲気圧力が低い(真空度が高い)ほど好ましい。具体的には、蒸着雰囲気圧力が $5 \times 10^{-4} Torr$ 以下であることが好ましく、 $5 \times 10^{-5} Torr$ 以下であることがより好ましい。また、気相堆積法による輝尽性蛍光体層の形成工程において、結晶の巨大化による画像の鮮鋭性の低下を防止する観点から、基板の温度は蒸発物質の融点より $100^\circ C$ 以上低いことが好ましい。輝尽性蛍光体層の層厚は、目的とする放射線画像交換パネルの放射線感度、輝尽性蛍光体の種類等によって異なるが、放射線吸収率の低下による放射線感度の低下を防止する観点から、 $30 \sim 1000 \mu m$ が好ましく、特に $50 \sim 500 \mu m$ が好ましい。輝尽性蛍光体層の層厚が小さすぎるときは、放射線吸収率が低下するため、放射線感度が悪くなり、また層厚が大きすぎる場合には輝尽励起光の横方向への広がりが増大するため画像の鮮鋭性が悪くなる。

【0019】図6および図7は、本発明の製造方法により形成された輝尽性蛍光体層4の柱状結晶5を模式的に示すものであり、柱状結晶5、5間にはほぼ均等にクラック6が形成され、各柱状結晶5は独立した構造になっ

ている。従って、輝尽励起光や輝尽発光が各柱状結晶5を鋭い指向性で進行するようになり、画像の鮮鋭性が向上する。さらに、本発明の製造方法により形成された輝尽蛍光体層の柱状結晶は、図7に示すaとbの平均の大きさが大きく異ならないので、放射線画像の読み取り方向が、横方向(図7のX方向)であっても、縦方向(図7のY方向)であっても、鮮鋭性がほぼ均しくなる。

【0020】柱状結晶5による輝尽励起光の散乱を防止し、また輝尽励起光の指向性の低下を防止して、MTF(画像の変調伝達関数)を良くするためには、柱状結晶5の大きさは、縦幅aおよび横幅b(図7参照)がそれぞれ $1 \sim 50 \mu m$ 程度がよく、特に $1 \sim 30 \mu m$ が好ましい。なお、図6、図7に示す柱状結晶形状は模式的に描かれたものであるため、これらの形に限定されるものではなく、また、蛍光体層全体にわたって一定の形あるいは一定の大きさである必要もない。

【0021】図8は、本発明の製造方法により製造された放射線画像交換パネルの具体的構成例を示し、7は保護層、8はスペーサ、9は低屈折率層である。基板1の材料としては、ガラス、セラミックス、各種高分子材料、金属等が用いられる。具体的には、石英ガラス、化学強化ガラス等のガラス、結晶化ガラス、アルミナあるいはジルコニアの焼結板等のセラミックス、あるいはセルローズアセテートフィルム、ポリエステルフィルム、ポリエチレンテレフタレートフィルム、ポリアミドフィルム、ポリイミドフィルム、トリアセテートフィルム、ポリカーボネートフィルム等のプラスチックフィルム、アルミニウム、アルミニウム-マグネシウム合金、鉄、ステンレス、銅、クロム等の金属シート等が挙げられる。基板の厚さは、その材質等によって異なるが、一般的には $100 \mu m \sim 5 mm$ が好ましく、取扱いの利便性から、特に $200 \mu m \sim 2 mm$ が好ましい。これらの基板の表面は滑面であってもよいし、輝尽性蛍光体層との付着性を向上させる目的で粗面としてもよい。また基板の大部分を滑面とし、周縁部のみを付着性を向上させる目的で粗面としてもよい。この場合、粗面とした周縁部は実質的に画像として用いない部分に止める方が、画質の均一化の点で好ましい。

【0022】保護層7は、輝尽性蛍光体層4を物理的にまたは化学的に保護するために設けられるものである。この保護層7は、図8のように低屈折率層9を介して輝尽性蛍光体層4に対向するように設けてもよいし、保護層用の塗布液を輝尽性蛍光体層上に直接塗布して形成してもよい。またあらかじめ別途形成した保護層を輝尽性蛍光体層上に接着してもよい。

【0023】保護層7を低屈折率層9を介して設ける場合、当該保護層7の構成材料としては、透光性が高く、シート状に成形できるものが使用される。保護層7は輝尽励起光および輝尽発光を効率よく透過するために、広い波長範囲で高い光透過率を示すことが望ましく、光透

過率は80%以上が好ましい。そのような材料としては、石英、ホウケイ酸ガラス、化学的強化ガラス等の板ガラスや、PET、延伸ポリプロピレン、ポリ塩化ビニル等の有機高分子化合物が挙げられる。ホウケイ酸ガラスは330nm~2.6μmの波長範囲で80%以上の光透過率を示し、石英ガラスではさらに短波長においても高い光透過率を示す。さらに、保護層7の表面に、MgF₂等の反射防止層を設けると、輝尽励起光および輝尽発光を効率よく透過すると共に、鮮鋭性の低下を小さくする効果もあり好ましい。保護層の厚さは、50~5000μmが好ましく、100~3000μmがより好ましい。

【0024】保護層7を輝尽性蛍光体層4上に直接設ける場合、当該保護層7の構成材料としては、酢酸セルロース、ニトロセルロース、ポリメチルメタクリレート、ポリビニルブチラール、ポリビニルホルマール、ポリカーボネート、ポリエステル、ポリエチレンテレフタレート、ポリエチレン、塩化ビニリデン、ナイロン等を用いることができる。また、この保護層6は、蒸着法、スパッタリング法等により、SiC、SiO₂、Si₃N₄、Al₂O₃等の無機物質を積層して形成してもよい。この場合には、保護層7の層厚は、0.1~100μmが好ましく、1~50μmがより好ましい。

【0025】低屈折率層9は、放射線画像の鮮鋭性をさらに向上させる観点から必要に応じて設けられるものである。具体的には、CaF₂（屈折率1.23~1.26）、Na₂AlF₆（屈折率1.35）、MgF₂（屈折率1.38）、SiO₂（屈折率1.46）等からなる層；エタノール（屈折率1.36）、メタノール（屈折率1.33）、ジエチルエーテル（屈折率1.35）等の液体からなる層；空気、窒素、アルゴン等の気体からなる層；真空層等のように屈折率が実質的に1である層；等から選択される。特に、気体層または真空層が好ましい。この場合、低屈折率層9の厚さは、通常0.05~3mmである。

【0026】低屈折率層9は、輝尽性蛍光体層4と密着していることが好ましく、従って、低屈折率層9が液体層、気体層、真空層の場合には、そのままでもよいが、低屈折率層9をCaF₂、Na₂AlF₆、MgF₂、SiO₂等を用いて保護層7の内面に設けた場合には、輝尽性蛍光体層4と低屈折率層9は例えば接着剤等により密着させればよい。

【0027】保護層7を輝尽性蛍光体層4に対して距離をおいて設ける場合には、基板1と保護層7との間に、輝尽性蛍光体層4を取囲むスペーサ8が設けられる。スペーサ8としては、輝尽性蛍光体層4を外周雰囲気から遮断した状態で保持することができるものであれば特に制限されず、ガラス、セラミックス、金属、プラスチック等を用いることができ、厚さは輝尽性蛍光体層の厚さ以上であることが好ましい。

【0028】本発明において「輝尽性蛍光体」とは、最初の光または高エネルギー放射線が照射された後に、光的、熱的、機械的、化学的または電気的等の刺激（輝尽励起）により、最初の光または高エネルギー放射線の照射量に対応した輝尽発光を示す蛍光体をいうが、実用的な面からは、光的刺激（輝尽励起）により輝尽発光を示す蛍光体が好ましく、波長が500nm以上1μm以下の輝尽励起光によって輝尽発光を示す蛍光体が特に好ましい。

【0029】輝尽性蛍光体層を構成する輝尽性蛍光体としては、以下のものを用いることができる。

(1) 特開昭48-80487号公報に記載のBaSO₄・xH₂O（ただし、Aは、Dy、Tb、Tmの少なくとも1種を表し、xは0.001≤x<1モル%を満たす数を表す。）で表される蛍光体。

(2) 特開昭48-80489号公報に記載のSrSO₄・xH₂O（ただし、Aは、Dy、Tb、Tmの少なくとも1種を表し、xは0.001≤x<1モル%を満たす数を表す。）で表されている蛍光体。

(3) 特開昭51-29889号公報に記載のNa₂SO₄・xH₂O、CaSO₄・xH₂O、BaSO₄・xH₂O等にMn、Dy、Tbの少なくとも1種を添加した蛍光体。

(4) 特開昭52-30487号公報に記載のBeO・xH₂O、LiF、MgSO₄・xH₂O、CaF₂等の蛍光体。

(5) 特開昭53-39277号公報に記載のLi₂O・xH₂O、Cu、Ag等の蛍光体。

【0030】(6) 特開昭54-47883号公報に記載のLi₂O・xH₂O（B、O₂）・xH₂O（ただし、xは2<x≤3を満たす数を表す。）・Li₂O・xH₂O（B、O₂）・xH₂O（ただし、xは2<x≤3を満たす数を表す。）等の蛍光体。

(7) 米国特許第3,859,527号明細書に記載のSrS：Ce、Sm、SrS：Eu、Sm、La、O₂、S：Eu、Sm、(Zn、Cd)S：Mn、X（ただし、Xはハロゲンを表す。）で表される蛍光体。

(8) 特開昭55-12142号公報に記載のZnS：Cu、Pb蛍光体。

(9) 同55-12142号公報に記載の一般式がBaO・xAl₂O₃・yEu₂O₃（ただし、xは0.8≤x≤10を満たす数を表す。）で表されるアルミニウムバリウム蛍光体。

(10) 同55-12142号公報に記載の一般式がM₂O・xSiO₂・yA（ただし、M₂は、Mg、Ca、Sr、Zn、Cd、Baを表し、Aは、Ce、Tb、Eu、Tm、Pb、Tl、Bi、Mnの少なくとも1種を表し、xは、0.5≤x<2.5を満たす数を表す。）で表されるアルカリ土類金属ケイ酸塩系蛍光体。

【0031】(11) 同55-12142号公報に記載の一般式が(Ba_{1-x-y}Mg_xCa_y)FX：eEu²⁺

(ただし、Xは、Br、Clの少なくとも1種を表し、

x, y, eは、それぞれ、 $0 < x + y \leq 0.6$ 、 $xy \neq 0$ 、 $10^{-6} \leq e \leq 5 \times 10^{-2}$ を満たす数を表す。)で表される蛍光体。

(12) 同55-12142号公報に記載の一般式が $LnOX : xA$ (ただし、Lnは、La, Y, Gd, Luの少なくとも1種を表し、Xは、Cl, Brの少なくとも1種を表し、Aは、Ce, Tbの少なくとも1種を表し、xは、 $0 < x < 0.1$ を満たす数を表す。)で表される蛍光体。

(13) 特開昭55-12145号公報に記載の一般式が $(Ba_{1-x}(M_1)_x)FX : yA$ (ただし、 M_1 は、Mg, Ca, Sr, Zn, Cdの少なくとも1種を表し、Xは、Cl, Br, Iの少なくとも1種を表し、Aは、Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Erの少なくとも1種を表し、x, yは、 $0 \leq x \leq 0.6$ 、 $0 \leq y \leq 0.2$ を満たす数を表す。)で表される蛍光体。

(14) 特開昭55-84389号公報に記載の一般式が $BaFX : xCe, yA$ (ただし、Xは、Cl, Br, Iの少なくとも1種を表し、Aは、In, Tl, Gd, Sm, Zrの少なくとも1種を表し、x, yは、 $0 < x \leq 2 \times 10^{-1}$ 、 $0 < y \leq 5 \times 10^{-2}$ を満たす数を表す。)で表される蛍光体。

(15) 特開昭55-160078号公報に記載の一般式が $M_1FX : xA : yLn$ (ただし、 M_1 は、Mg, Ca, Ba, Sr, Zn, Cdの少なくとも1種を表し、Aは、BeO, MgO, CaO, SrO, BaO, ZnO, Al₂O₃, Y₂O₃, La₂O₃, In₂O₃, SiO₂, TiO₂, ZrO₂, GeO₂, SnO₂, Nb₂O₅, Ta₂O₅, ThO₂の少なくとも1種を表し、Lnは、Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sm, Gdの少なくとも1種を表し、Xは、Cl, Br, Iの少なくとも1種を表し、x, yは、 $5 \times 10^{-4} \leq x \leq 0.5$ 、 $0 < y \leq 0.2$ を満たす数を表す。)で表される希土類元素付活2価金属フルオロハライド蛍光体。

【0032】(16) 同55-160078号公報に記載の一般式が $ZnS : A, (Zn, Cd)S : A, CdS : A, ZnS : A, X, CdS : A, X$ (ただし、Aは、Cu, Ag, Au, Mnのいずれかを表し、Xは、ハロゲンを表す。)で表される蛍光体。

(17) 特開昭59-38278号公報に記載の一般式【I】 $xM, (PO)_2, \cdot NX, : yA$
一般式【II】 $M, (PO)_2, \cdot yA$

(式中、M, Nは、それぞれ、Mg, Ca, Sr, Ba, Zn, Cdの少なくとも1種を表し、Xは、F, Cl, Br, Iの少なくとも1種を表し、Aは、Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sb, Tl, Mn, Snの少なくとも1種を表し、x, yは、 $0 < x \leq 6$ 、 $0 \leq y \leq 1$ を満たす数を表

す。)で表される蛍光体。

(18) 特開昭59-155487号公報に記載の一般式【III】 $nReX, \cdot mAX', : xEu$
一般式【IV】 $nReX, \cdot mAX', : xEu, ySm$

(式中、Reは、La, Gd, Y, Luの少なくとも1種を表し、Aは、Ba, Sr, Caの少なくとも1種のアルカリ土類金属を表し、X, X'は、F, Cl, Brの少なくとも1種を表し、x, yは、 $1 \times 10^{-4} < x < 3 \times 10^{-1}$ 、 $1 \times 10^{-4} < y < 1 \times 10^{-1}$ を満たす数を表し、 n/m は、 $1 \times 10^{-2} < n/m < 7 \times 10^{-1}$ を満たす数を表す。)で表される蛍光体。

(19) 特開平2-58593号公報に記載の一般式 $aBaX, \cdot (1-a)BaY, : bEu^{2+}$

(式中、X, Yは、それぞれ、F, Cl, Br, Iの少なくとも1種を表し、 $X \neq Y$ であり、a, bは、 $0 < a < 1$ 、 $10^{-3} < b < 10^{-1}$ を満たす数を表す。)で表される蛍光体。

(20) 特開昭61-72087号公報に記載の一般式 $M_1X \cdot aM_{11}X', \cdot bM_{111}X'', : cA$

(ただし、 M_1 は、Li, Na, K, Rb, Csの少なくとも1種のアルカリ金属を表し、 M_{11} は、Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Niの少なくとも1種の2価の金属を表し、 M_{111} は、Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga, Inの少なくとも1種の3価の金属を表し、X, X', X''は、F, Cl, Br, Iの少なくとも1種のハロゲンを表し、Aは、Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu, Mgの少なくとも1種の金属を表し、a, b, cは、 $0 \leq a < 0.5$ 、 $0 \leq b < 0.5$ 、 $0 < c \leq 0.2$ を満たす数を表す。)で表されるアルカリハライド蛍光体。

【0033】本発明においては、アルカリハライド蛍光体が蒸着法に好適であることから特に好ましく用いることができる。ただし、本発明においては、以上の蛍光体に限定されず、放射線を照射した後、輝尽励起光を照射した場合に輝尽発光を示す蛍光体であって、気相堆積できるものであれば、その他の蛍光体をも用いることができる。

【0034】図9は本発明の方法により製造された放射線画像変換パネルを用いて構成された放射線画像変換装置の一例の概略を示し、10は放射線発生装置、11は被写体、12は放射線画像変換パネル、13は輝尽励起光源、14は放射線画像変換パネル12より放射された輝尽発光を検出する光電変換装置、15は光電変換装置14で検出された信号を画像として再生する再生装置、16は再生装置15により再生された画像を表示する表示装置、17は輝尽励起光と輝尽発光とを分離し、輝尽発光のみを透過させるフ

ィルターである。この放射線画像変換装置においては、放射線発生装置10からの放射線は被写体11を通して放射線画像変換パネル12に入射する。この入射した放射線は放射線画像変換パネル12の輝尽性蛍光体層に吸収され、そのエネルギーが蓄積され、放射線透過像の蓄積像が形成される。次に、この蓄積像を輝尽励起光源13からの輝尽励起光で励起して輝尽発光として放射させる。放射される輝尽発光の強弱は、蓄積された放射線エネルギー量に比例するので、この光信号を例えば光電子増倍管等の光電変換装置14で光電変換し、再生装置15によって画像として再生し、表示装置16によって表示することにより、被写体11の放射線透過像を観察することができる。【0035】以下、さらに具体的な実施例について説明するが、本発明はこれらの実施例に限定されるものではない。

【実施例1】図1に示すように、厚さが0.5mm、大きさが100mm×100mmで、表面が平滑なアルミニウム板からなり、 1×10^{-3} Torr以下の雰囲気圧力下で250℃の温度に加熱された基板1を水平な姿勢で固定配置し、この基板1の被蒸着面1Aの下方側において輝尽性蛍光体材料(RbBr: 1×10^{-4} Tl)からなる蒸発源2を、基板1の被蒸着面1Aの法線方向を軸として公転できるように配置した。蒸発源2を被蒸着面1Aの法線方向を軸として水平面内で公転させながら、電子ビームにより蒸発源2を蒸発させて蒸気流を形成し、基板1の被蒸着面1Aに輝尽性蛍光体層を形成した。ただし、蒸気流の流線方向Aと、基板の被蒸着面中央部分での法線方向との交角(鋭角)θは45°に設定した。得られた輝尽性蛍光体層を電子顕微鏡により観察したところ、縦幅aの平均が7μm、横幅bの平均が11μm、膜厚が250μmの微細な柱状結晶から構成されていることが確認できた。この輝尽性蛍光体層上に、乾燥した窒素ガスからなる低屈折率層を介してガラス板からなる保護層を設けて、放射線画像変換パネル1を製造した。

【0036】【実施例2】図2に示すように、実施例1と同様の輝尽性蛍光体材料からなる蒸発源2を固定配置し、この蒸発源2の上方側位置において、実施例1と同様の基板1を水平面内においてその中央における法線方向Bを中心にして自転できるように配置した。基板1を当該法線方向Bを軸として水平面内で自転させながら、電子ビームにより蒸発源2を蒸発させて蒸気流を形成し、基板1の被蒸着面1Aに輝尽性蛍光体層を形成した。ただし、交角θは45°に設定した。得られた輝尽性蛍光体層を電子顕微鏡により観察したところ、縦幅aの平均が7μm、横幅bの平均が11μm、膜厚が250μmの微細な柱状結晶から構成されていることが確認できた。以下実施例1と同様にして放射線画像変換パネル2を製造した。

【0037】【実施例3】図3に示すように、実施例1

と同様の輝尽性蛍光体材料からなる蒸発源2を固定配置し、この蒸発源2の上方側位置において、実施例1と同様の基板1を傾斜面内においてその中央における法線方向Bを中心にして自転できるように配置した。基板1を当該法線方向Bを軸として傾斜面内で自転させながら、電子ビームにより蒸発源2を蒸発させて蒸気流を形成し、基板1の被蒸着面1Aに輝尽性蛍光体層を形成した。ただし、交角θは40°に設定した。得られた輝尽性蛍光体層を電子顕微鏡により観察したところ、縦幅aの平均が8μm、横幅bの平均が11μm、膜厚が250μmの微細な柱状結晶から構成されていることが確認できた。以下実施例1と同様にして放射線画像変換パネル3を製造した。

【0038】【実施例4】図4に示すように、実施例1と同様の輝尽性蛍光体材料からなる円環状の蒸発源2を水平な姿勢で固定配置すると共に、円環状の蒸発源2の中央部に電子ビーム発生装置3を配置し、この蒸発源2の上方側位置において、実施例1と同様の基板1を水平な姿勢で固定配置した。電子ビーム発生装置3よりの電子ビーム3Aの照射位置を、円環状の蒸発源2の周に沿って順次に移動させて蒸発源2を蒸発させて蒸気流を形成し、基板1の被蒸着面1Aに輝尽性蛍光体層を形成した。ただし、交角θは40°に設定した。得られた輝尽性蛍光体層を電子顕微鏡により観察したところ、縦幅aの平均が8μm、横幅bの平均が11μm、膜厚が250μmの微細な柱状結晶から構成されていることが確認できた。以下実施例1と同様にして放射線画像変換パネル4を製造した。

【0039】【比較例1】図10に示すように、実施例1と同様の輝尽性蛍光体材料からなる蒸発源2を固定配置し、この蒸発源2の上方側位置において、実施例1と同様の基板1を交角θが40°となる傾斜面内において自転できないように固定配置した。電子ビームにより蒸発源2を蒸発させて蒸気流を形成し、基板1の被蒸着面1Aに輝尽性蛍光体層を形成した。得られた輝尽性蛍光体層を電子顕微鏡により観察したところ、縦幅aの平均が6μm、横幅bの平均が26μm、膜厚が250μmの幅広い板状結晶から構成されていることが確認できた。以下実施例1と同様にして放射線画像変換パネルaを製造した。

【0040】【比較例2】図11に示すように、実施例1と同様の輝尽性蛍光体材料からなる蒸発源2を固定配置し、この蒸発源2の上方側位置において、実施例1と同様の基板1を水平面内においてその中央における法線方向Bを中心にして自転できるように配置した。ただし、蒸発源2は基板1の被蒸着面1Aの中央における法線方向の直下に配置した。基板1を当該法線方向Bを軸として水平面内で自転させながら、電子ビームにより蒸発源2を蒸発させて蒸気流を形成し、基板1の被蒸着面1Aに輝尽性蛍光体層を形成した。得られた輝尽性蛍光

体層を電子顕微鏡により観察したところ、柱状結晶になっていないことが確認できた。以下実施例1と同様にして放射線画像変換パネルbを製造した。

【0041】評価

以上のようにして製造した放射線画像変換パネル1~4と比較用の放射線画像変換パネルa、bをそれぞれ用いて、図9に示す構成の放射線画像変換装置を用いて、実際に放射線画像を形成する試験を行い、下記のようにして放射線画像の鮮鋭性を調べた。

【0042】鮮鋭性

放射線画像変換パネルにCTFチャートを貼付けた後、管電圧80kV_{r.p.}のX線を10mR（管球からパネルまでの距離：1.5m）照射した後、半導体レーザー光（発振波長：780nm、ビーム径：100μm）で走査して輝尽励起し、CTFチャート像を輝尽性蛍光体層から放射される輝尽発光として読取り、光検出器（光電子増倍管）で光電変換して画像信号を得た。この信号値により、画像の変調伝達関数（MTF）を調べ、放射線画像の鮮鋭性を相対値で評価した。なお、MTFは、空間周波数が3サイクル/mmの時の値である。以上の結果を後記表1に示した。

【0043】

【表1】

	画像の鮮鋭性（％）	
	X方向	Y方向
実施例1	44	40
実施例2	43	40
実施例3	42	40
実施例4	42	39
比較例1	45	35
比較例2	28	28

【0044】表1から明らかなように、本発明の製造方法によれば、放射線画像の鮮鋭性が優れ、しかも鮮鋭性が読取り方向によってあまり変化せず、画質の均一性の*

*点でも良好な放射線画像変換パネルが得られる。

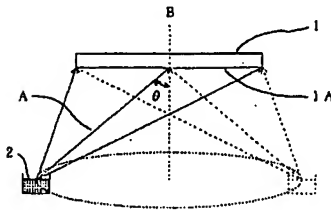
【0045】

【発明の効果】以上詳細に説明したように、本発明によれば、幅の狭い精度の高い柱状結晶からなる輝尽性蛍光体層を形成することができ、放射線画像の鮮鋭性が優れ、しかも読取り方向による鮮鋭性の変化が小さいため画質の均一性の点でも良好な放射線画像変換パネルを製造することができる。

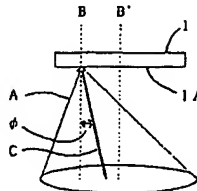
【図面の簡単な説明】

- 10 【図1】輝尽性蛍光体層の製造例を示す図である。
 【図2】輝尽性蛍光体層の他の製造例を示す図である。
 【図3】輝尽性蛍光体層の他の製造例を示す図である。
 【図4】輝尽性蛍光体層の他の製造例を示す図である。
 【図5】蒸気流ベクトルの総和ベクトルと被蒸着面の法線方向との交角φの説明図である。
 【図6】柱状結晶からなる輝尽性蛍光体層を模式的に示した断面図である。
 【図7】柱状結晶からなる輝尽性蛍光体層を模式的に示した斜視図である。
 20 【図8】放射線画像変換パネルの具体的構成例を示した断面図である。
 【図9】放射線画像変換装置の一例の概略を示した説明図である。
 【図10】比較例1の説明図である。
 【図11】比較例2の説明図である。
 【符号の説明】
- | | | | |
|----|-----------|----|------------|
| 1 | 基板 | 2 | 蒸気源 |
| 3 | 電子ビーム発生装置 | 4 | 輝尽性蛍光体層 |
| 5 | 柱状結晶 | 6 | クラック |
| 7 | 保護層 | 8 | スペーサ |
| 9 | 低屈折率層 | 10 | 放射線発生装置 |
| 11 | 被写体 | 12 | 放射線画像変換パネル |
| 13 | 輝尽励起光源 | 14 | 光電変換装置 |
| 15 | 再生装置 | 16 | 表示装置 |
| 17 | フィルター | | |

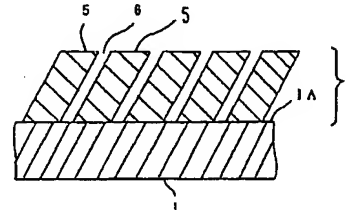
【図1】



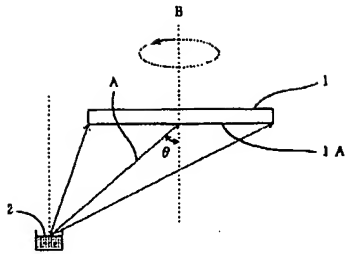
【図5】



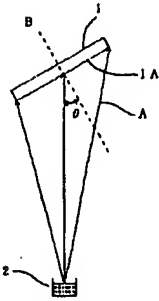
【図6】



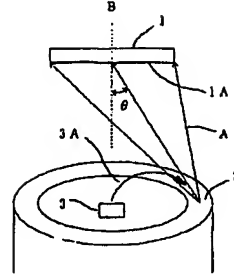
【図2】



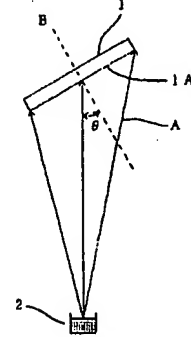
【図3】



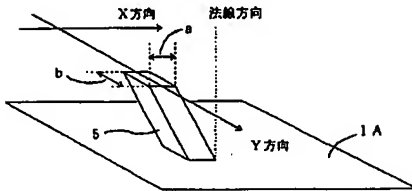
【図4】



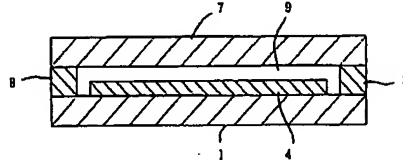
【図10】



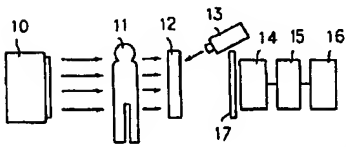
【図7】



【図8】



【図9】



【図11】

